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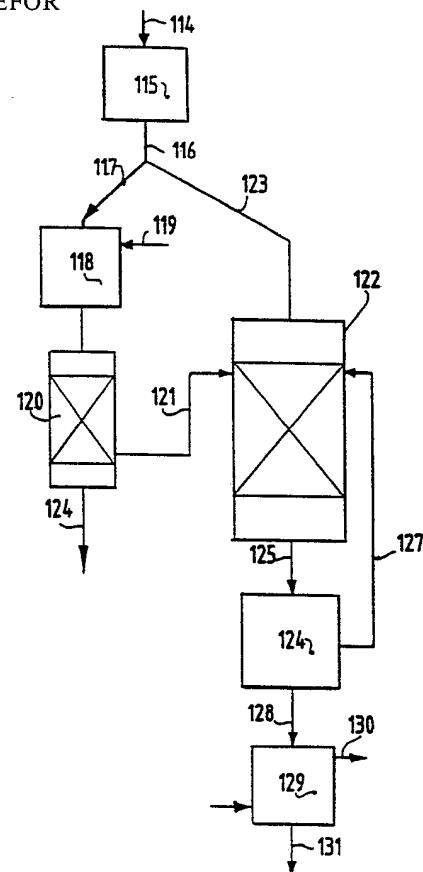
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(54) Title: METHODS FOR PROCESSING MANURE AND A DEVICE THEREFOR

(57) Abstract

The present invention relates to a method for preparing a granular fertilizer from manure. The present invention relates further to the treating of manure condensate that results in the processing of manure, to a method for the synthesis of organic compounds, such as amino acids, namely L-lysine and L-methionine, from manure, to a method for refining volatile, organic compounds from manure, and to a specific method and device for treating manure.



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Methods for processing manure and a device therefor

The present invention relates to a method for preparing a granular fertilizer from manure. The present invention relates further to the treating of manure condensate that results in the processing of manure, to a method for the 5 synthesis of organic compounds, such as amino acids, namely L-lysine and L-methionine, from manure, to a method for refining volatile, organic compounds from manure, and to a specific method and device for treating manure.

In the conversion processes of manure it is important 10 that as much as possible valuable products are separated from the manure. In these conversion processes most attention is paid to the separation of solids from the manure, which solids after drying may be used as a substitute for artificial fertilizer.

15 A known manure converting process is the so called Promest process, wherein first the manure is fermented in a fermentation installation, in order to produce biogas. Subsequently solids are removed from the manure fermented, which solids form after drying as manure cake a valuable 20 product. Due to the fermentation the manure cake comprises a relative low amount of organic compounds. These organic compounds in combination with the mineral nutrients, nitrogen, phosphorus and potassium, incorporated in the fertilizer result in a positive difference of the fertilizer 25 over artificial fertilizer.

The invention has for its object to provide a fertilizer which is agronomically improved over artificial fertilizer, so that as will be illustrated below the dose of fertilizer may be reduced to that of artificial fertilizer.

30 According to the invention this is obtained in that the method according to the invention for preparing a granular fertilizer from manure, comprises the steps of:

- i) acidifying the manure;

ii) dehydrating the acidified manure and evaporating the carrier liquid; and

iii) forming granules from the fertilizer obtained.

By acidifying the manure, preferably already at the 5 farm, the biological degradation of the organic substances present in the manure, is substantially avoided. Accordingly the fertilizer according to the invention will comprise a relatively high percentage of organic substances, generally more than 30 to 40%, preferably about 50% organic substances.

10 Next to this the emission of ammonia is strongly reduced.

For example the manure may be acidified using nitric acid. But for safety reasons sulphuric acid is preferred, whereby the formation of ammonium nitrate that might be explosive, is avoided. In using sulphuric acid in the 15 acidification the composition of the active nutrients nitrogen, phosphorus and potassium in the fertilizer is 9-3-6. Using sulphuric acid in the acidification, the composition of these active nutrients nitrogen, phosphorus and potassium is 6-3-6. An agronomical study showed, that the fertilizer 20 possess a phosphate effect which is equal to that of artificial fertilizer, whereas the nitrogen effect (mineral and organic nitrogen) is about 70% of that of artificial fertilizer.

Preferably the acidification is carried out using a 25 mixture of nitric acid and sulphuric acid because under particular conditions the acidification using this mixture improves the agronomical value of the fertilizer. For example the acidification may be carried out using a mixture of which the nitric acid to sulphuric acid ratio is 30-50:70-50. More 30 preferably the nitric acid to sulphuric acid ratio is 35-45:65-55.

Dependent on the type of manure and on the solid content of the manure, the amount of acid added is generally sufficient to result in a pH increase of 3.5-5.5, more 35 preferably to 4-5, particularly to 4.1-4.3. Generally the amount of acid added is 1-10% by weight based on the weight of the manure. More preferably the amount added is 1-5% by weight, conventionally 3% by weight.

Additives may be added to the fertilizer in order to adjust the composition of the active nutrients and nitrogen, phosphorus and potassium to the fertilization advice, the additives comprise sulphates, nitrates and potassium salts.

5 Because usually the fertilizer obtained is in a powder form, it is preferred to granulate the fertilizer. In principle the fertilizer granulates spontaneously, but the granulation may be carried out within narrow granulate-sized distributions when preferably granulation promoting agents 10 are added. These granulation promoting agents comprise for instance chalk, molasses, carboxymethyl cellulose and bentonite. In fact these additives are binders which bind the fertilizer granules to an agglomerate.

In order to avoid the emission of large volumes of air 15 when the agglomerate formed is dried, it is preferred to dry the agglomerate using vacuum cooling. Accordingly it is possible to save significantly on the amount of air to be discharged, if necessary the air must be purified, but moreover the odour emission is substantially reduced, and the 20 condensation water formed may be purified at relatively low costs prior to discharge.

Preferably the manure is dehydrated according to the so called Greenfield process (US-3.855.079, US-4.270.974 and US-4.608.120). According to this known process a non-volatile 25 oil is added to the manure and the oil slurry formed is dehydrated by evaporation using heat, whereafter the oil is removed from the solids by evaporation at a temperature of 140-160°C. Due to this high evaporation temperature weed seeds present in the manure are killed, and a sterilization 30 takes place which allows a longterm storage of the fertilizer or fertilizer granules. Another important advantage is that germs containing manure, such as swine fever, may be processed because all germs are killed in the sterilization step.

35 In this respect it is an additional advantage, that after granulation hair which may be present in the manure may be easily removed by sieving.

The granulate formed has a solid content of more than 80% preferably more than 85%, more preferably more than 90%. Generally the granulate comprises:

5 $\text{NH}_4\text{-N1}$ - 3 % by weight
 $\text{NO}_3\text{-N1,5}$ - 3,5 % by weight
 N-total5 - 9 % by weight
 $\text{P}_2\text{O}_5\text{-total12}$ - 5 % by weight
 $\text{K}_2\text{O}\text{-total3}$ - 10 % by weight

The method according to the invention may be used with 10 many types of manure, such as manure which originates from cattle farm, swine farm, poultry farm and the like. Generally the manure may have a solid content of more than 7%, but the method according to the invention is particularly suitable for manure having a higher solid content, such as preferably 15 at least 10%, and more preferably to more than 14%.

Accordingly the advantage is obtained, that in a central manure processing a smaller amount of manure is to be transported. Moreover the addition of acid at the farm results in a remarkably reduced emission of ammonia.

20 Hereafter the method according to the invention will be illustrated further with reference to an embodiment in which also the agronomical value of the fertilizer prepared is compared to that of artificial fertilizer.

Bulky waste is removed by sieving from swine manure 25 which prior to storage is acidified using nitric acid or a mixture of nitric acid and sulphuric acid (40/60) (w/w), whereby the pH of the manure is lowered to pH 4.2. The manure acidified was mixed with a water insolvable, liquid paraffin having a boiling point of about 180°C. This mixture of manure 30 and paraffin was dehydrated by evaporation. The vapor formed was condensated in a condenser. The concentrated liquid mixture of manure and paraffin was added to a heating vessel, in which at a temperature of about 180-190°C the paraffin was removed by evaporation. If necessary remainder paraffin may 35 be removed from the fertilizer obtained by steam stripping. After drying the fertilizer obtained has a residual moisture content of about 1.5% and a fineness such that about 28% of the fertilizer has a particle size smaller than 100 μm . The bulk weight is about 500 g/l.

Subsequently the fertilizer is granulated. Thereto the fertilizer, if necessary additives and granulation promoting agent are added to a granulation drum, in which the fertilizer is granulated to a granulate having a particle 5 size distribution which very substantially within 0.5-8 mm.

Subsequently the granulate is sieved in order to remove hair and the like. Finally the granulate is classified.

The granulate formed generally has a moisture content of 25-35%, preferably 32-36%. The temperature of the 10 granulate is dependent on the granulation process used, but for instance lies between 80-100°C.

Subsequently the granulate is added to a vacuum cooling unit, in which the moisture access is readily evaporated by reducing the pressure to about 20 mBar, and the temperature 15 of the granulate decreases. If the granulate to be dried has a temperature which is not sufficiently high, the granulate may be conditioned by adding an extra amount of steam.

Using this vacuum cooling technique the amount of air necessary for drying the granulate is substantially reduced, 20 whereas the granulate has an optimal abrasion resistance, hardness and capability. It is noted that for a sufficient fast drying of the granulate, it is preferred that the granulate has a diameter which lies between 1 and 8 mm. Finally if necessary, the granulate may be post-dried.

25 The table below shows a number of granulation experiments using fertilizer which is acidified using a mixture of 40/60 nitric acid/sulphuric acid.

The fertilizer granulates obtained from manure that is acidified with nitric acid (hereafter referred to as 30 fertilizer N) and acidified using a mixture of 40/60 nitric acid/sulphuric acid (hereafter referred to as fertilizer S) are studied for their agronomical value, using artificial fertilizer as a reference.

Table 2 shows the composition of the fertilizer 35 granulates used.

The experiments are performed on clay soil and on sand soil. On clay soil the crop was consumption potatoes and on sand soil the crop was industrial potatoes.

For each type of soil five fertilizers-N-steps were used, which varied from 0 to 280 kg nitrogen/ha pro year. Based on a soil test the fertilization advice for clay soil was 220 kg nitrogen and for sand soil 210 kg nitrogen.

5 During the growth season the crop showed very rapidly remarkable differences in colour. Crop grown on fertilizer products had a colour which on average was comparable to crop fertilized with 140 kg nitrogen/ha.

10 Figure 1 and 2 show the results of the field experiments on clay soil for the nitrogen content (in % solids) and nitrogen uptake (in kg/ha) at a nitrogen dose using artificial fertilizer (0-280 kg/ha) and by N-fertilizer and S-fertilizer. The figures 3 and 4 show similar results in field experiments on sand soil.

15 From these results it is apparent that a mineral nitrogen dose of 100 kg/ha in the form of fertilizer corresponds to a nitrogen dose of 140 kg/ha in the form of artificial fertilizer. Accordingly the mineral load of the soil is lower.

20 In the experiments on clay soil using consumption potatoes it was apparent that using the N-fertilizer and S-fertilizer the yield of potatoes in ton/ha in comparison to that using artificial fertilizer (59.1 ton/ha) is increased to 42.2 and 67.2 ton/ha, respectively.

25 For industrial potatoes on sand soil the yield in comparison to that using artificial fertilizer (46.0 ton/ha) is increased to 48.4 en 48.5 ton/ha, respectively. The weight of crop paid for was, in comparison to 67.6 ton/ha using artificial fertilizer, 67.8 and 66.8 ton/ha, respectively.

30 These experiments further show that nitrogen present in the fertilizer is remarkably active, whereby not only mineral nitrogen but also organic nitrogen is active. This may explain the lower dose of fertilizer according to the invention compared to that of artificial fertilizer, in order 35 to obtain similar yield results.

For the cost-effectiveness of processing processes for manure it is important to separate as many valuable products as possible from the manure. Not only the sale price of these valuable products is of importance but also the price that

has to be paid for treating the resulting waste flows which can only be discharged into the environment after treatment.

A process for processing manure is only cost-effective from an economic point of view if the forming of valuable products is maximalized while at the same time the forming of waste flows is minimalized. For the waste flows this means that the composition of the waste flows must be such that they can be treated at the lowest possible cost. These treating costs can be further reduced if during treatment products result which can contribute to the cost-effectiveness of the total processing process for manure. In this case the production of biogas is given particular attention.

A first, known processing process for manure is the so-called Promest process, wherein the manure is fermented in a fermentation installation prior to further processing and biogas is formed. Subsequently separated from the fermented manure are the solids which, after drying, provide a manure cake. As a consequence of the fermentation the waste flows contain a small quantity of organic compounds, but the quantity of inorganic compounds is relatively high, whereby the treating costs of the formed waste water flows are comparatively high. Moreover, the total manure volume is in principle subjected to a fermentation which is therefore voluminous on account of the long duration time in the fermentation installation.

A second known processing process is the so-called Greenfield process (US-3.855.079, US-4.270.974 and US-4.608.120). According to this known processing process an organic carrier liquid is added to the manure, whereafter the mixture of manure and carrier liquid is dehydrated by evaporation, whereafter the formed vapour is condensed to condensate. The composition of this condensate is such that this condensate can only be discharged into the environment after treatment.

A biological treatment of this condensate seems virtually impossible because of the composition thereof.

Firstly, this condensate contains very few nutrients and minerals, which are necessary for a biological degradation.

Secondly, the condensate will contain toxic components derived from the manure, such as ammonia and phenolic compounds; and

5 Thirdly, the condensate contains residues of the used organic carrier liquid which will have a braking effect on the bacterial degradation processes, or result in flushing of the biomass out of the treatment reactor.

Surprisingly, however, it has been found that the condensate, despite its composition, which would make a bacterial treatment expensive, can be treated at relatively low 10 treating cost, if the condensate is subjected successively to an anaerobic treatment followed by an aerobic treatment.

The invention therefore relates to a method for processing manure, which method comprises the steps of:

15 i) adding an organic carrier liquid to the manure;
ii) concentrating the mixture of manure and carrier liquid;
iii) condensing the formed vapour;
iv) anaerobic treating of the condensate; and
20 v) aerobic treating of the effluent from the aerobic treatment.

If the manure is acidified, preferably prior to concentrating thereof, but more preferably immediately after the production of the manure, that is, on the farm, the 25 amount of ammonia in the manure remains high, thus avoiding ammonia emission. Because of the low pH, undesired fermentation will moreover occur as little as possible, whereby the organic material present is not degraded, and this organic material, which passes over into the condensate via the vapour phase, can function therein as an essential carbon source. The supplement of a carbon source can thereby be dispensed with to a very considerable extent.

If in preference a portion of the effluent from the anaerobic treatment is recirculated and mixed with condensate 35 for treating, at the beginning of the anaerobic treating the adding of a base in order to raise the pH of the condensate to a pH necessary for anaerobic treatment can be omitted. The effluent of the anaerobic treatment in any case has a higher pH through the degradation of the fatty acids present in the

condensate. In preference 20-90%, preferably 30-80%, and more preferably 40-80% of the effluent is recirculated.

In order to enable forming to a sufficient degree in the anaerobic treatment of new biomass, it is recommended 5 that a nutrient preparation is added to the condensate such as molasses and vinasse.

It has been found that the condensate composition is such that there is a primary requirement for nitrogen. In the case of a nitrogen requirement the nutrient preparation 10 therefore supplements such that the nitrogen requirement is provided, and this at least for a nitrogen requirement of at least 50g/m³, preferably 60g/m³, and more preferably 70-80 g/m³.

Another nutrient requirement is the need for phosphor. 15 If a phosphor requirement occurs a nutrient preparation supplements therefor, for instance for a phosphor requirement of at least 10g/m³, preferably 15g/m³, and more preferably 20g/m³.

If as a consequence of its composition the condensate 20 requires a trace element supplement, this nutrient preparation preferably also contains trace elements. In diminishing requirement of trace elements the nutrient preparation may contain iron, nickel, cobalt, manganese, zinc, molybdenum and copper.

25 If necessary, micro-nutrients such as sulphur, potassium, calcium and magnesium may also be added.

It has been found that with an anaerobic treatment at a temperature of 30-40°C, preferably 35-40°C, and a pH 6-8, preferably 7, a COD (Chemical Oxygen Demand) processing yield 30 can be achieved of more than 80%, preferably 85%, more preferably 90%, such as 90-95%.

Since the condensate contains substantially no sugars, amino acids and alcohols, but mainly volatile fatty acids, hydrogen and carbon dioxide, of particular importance for the 35 anaerobic degradation are obligatory hydrogen producing acetogenic bacteria, acetic acid splitting, methane producing bacteria and hydrogen oxidizing, methane producing bacteria. This specific composition requires a specific biomass. It has been found that sludge used in the treatment of waste water

from alcohol preparation and/or paper preparation is suitable as oculant sludge. This sludge is preferably adapted to the specific presence of relatively large quantities of propionic acid and isovaleric acid. Preferably used therefore is sludge 5 that is adapted to the degradation of C_n fatty acids, wherein n≥2. Found to be particularly suitable is sludge derived from the treating of waste water that is released during the production of sugar from sugar beets.

Since the anaerobic treatment leaves ammonia present in 10 the condensate undisturbed and the chemical oxygen demand (COD) of the condensate is not completely removed, an aerobic after-treatment is performed wherein the residual carbon source is used in the nitrification and subsequent denitrification, whereby nitrogen containing compounds, mainly 15 ammonia, are eventually converted into nitrogen. With respect to the aerobic after-treatment the method according to the invention is therefore characterized in that the effluent originating from the anaerobic treatment is denitrified in a denitrification unit and nitrified in a nitrification unit, 20 and wherein a portion of the sludge-influent mixture from the nitrification unit is recirculated to the denitrification unit. Because the sludge-influent mixture from the nitrification unit is fed back to the denitrification unit, nitrification and denitrification can take place 25 simultaneously in the same installation, while optimal use can nevertheless be made in the denitrification of the carbon source (COD) still present in the influent. The recirculation ratio, that is, the recirculated flow over the flow to the nitrification unit, amounts generally to 10-30, more 30 preferably 15-25, such as 20. The recirculation ratio is dependent on the composition of the effluent, particularly the concentrations of ammonia and other nitrogen compounds present, but specifically on the carbon source present.

If this carbon source is not present in the influent in 35 sufficient quantity, it has been found, surprisingly, that crude condensate can be used for supplementing the carbon source without the denitrification and nitrification being adversely influenced thereby.

Depending on the composition of the influent and the crude condensate the influent may contain 1-20% crude condensate, more preferably 5-20% and such as in practice 10-15%.

5 Sludge deriving from the nitrification unit is preferably pre-mixed with the influent. The micro-organisms present in the sludge are thus exposed to high substrate concentrations, whereby the floc formation is promoted. This 10 floc forming, the growing of micro-organisms to agglomerates, 15 is very important for the later separating of the formed biomass (sludge) from the treated liquid in the settling tank.

If the anaerobic treatment and the aerobic treatment according to the invention are performed optimally, the condensate can be treated to a dischargeable liquid, and the 15 treating method according to the invention achieves a treatment yield that is greater than 90% BOD (biological oxygen demand), but the treatment yield is frequently greater than 95% BOD, and in practice the treatment yield amounts to 97-20 99% BOD.

The method according to the invention will be described hereinafter with reference to an embodiment in a treating installation which is depicted schematically in flow diagrams in figures 5 (anaerobic treatment) and 6 (aerobic treatment).

25 Pig manure with the composition indicated in table 3 is acidified with nitric acid to circa pH 4.

Depending on the degree of acidification the ammonia content of the condensate amounts generally to between 500 and 2000 ppm.

30 The acidified manure is mixed with a water-insoluble liquid paraffin with a boiling point of about 180°C. The mixture of manure and paraffin is concentrated in a concentrator, wherein the vapour formed is condensed in a condenser. Resulting from this heat treatment of a duration 35 of at least 30 minutes is a condensate that can be considered as a sterilized liquid.

Added to the condensate prior to treating in the installation in figure 5 are a macro/micro-nutrient solution and a trace element solution. The macro/micro-nutrient solu-

tion had the following composition: KH_2PO_4 28.3 g/l, $(\text{NH}_4)_2\text{SO}_4$ 28.3 g/l, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ 24.5 g/l, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 25 g/l, KCl 45 g/l, yeast extract 3.3 g/l, in demineralized water; the trace element solution had the following composition: $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ 5 2000 mg/l, H_3BO_3 50 mg/l, ZnCl_2 50 mg/l, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ 30 mg/l, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ 500 mg/l, $(\text{NH}_4)_6\text{MO}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ 50 mg/l, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ 90 mg/l, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ 2000 mg/l, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 92 mg/l, $\text{Na}_2\text{SeO}_5 \cdot 5\text{H}_2\text{O}$ 164 mg/l, EDTA 1000 mg/l, resazurine 200 mg/l, HCL 36% 1 ml/l, in demineralized water. The composition of the condensate that 10 is fed to the installation of figure 5 is also stated in table 3.

The condensate is fed to the anaerobic treatment installation that is shown in figure 5.

The condensate is fed via a conduit 1 having a pump 2 15 accommodated therein to a feed conduit 3 of the reactor 4. The reactor 4 is of the so-called upflow anaerobic sludge-bed type (UASB). The biomass present in the reactor 4 is formed from an oculate with granular sludge derived from a central treating installation of waste water from the paper industry.

20 Via a riser pipe 6 that is closable with a valve 5 effluent leaves the reactor 4 via a conduit 7. A portion of this effluent is recirculated via the recirculation conduit 8 wherein a pump 9 is arranged. The recirculation factor amounted to 10. Thus obtained was a superficial liquid speed 25 of 0.15-0.6 m per hour.

The anaerobic treatment was performed at a temperature of 35°C while formed biogas was discharged via a conduit 10 for further processing and later generating of calorific heat.

30 In the installation shown in figure 5 the hydraulic duration time was 24 hours. The specific sludge load amounted to 0.14 kg COD/kg VSS.day, at a volume load of 7.3 kg COD/ m^3 . day. 5 kg of sodium hydrogen carbonate per m^3 was moreover added to the condensate.

35 After stabilization a COD removal yield of 90-95% was obtained (after separation of suspended material from the effluent).

It can be seen from these experimental conditions that the composition of the supplemented condensate is sufficient

to meet the nutrient requirements for nitrogen, phosphorus, sulphur, potassium, calcium, magnesium and iron.

With reference to figure 6, the influent derived from the anaerobic treatment shown in figure 5 is added to a 5 mixing tank 10 to which crude condensate is also added via the conduit 10 in a quantity such that the influent eventually contains 10% crude condensate. The compositions of the crude condensate, the anaerobically treated condensate and the anaerobically treated condensate + 10% crude 10 condensate (influent) are shown in table 4.

The influent is fed to a contact tank 13 wherein the influent is mixed with sludge coming from the settling tank 14 and is recirculated via a conduit 15 in which is arranged a pump 16. The influent-sludge mixture is fed to a 15 denitrification unit 14 in which nitrogen oxides (NO_2^- and NO_3^-) are converted into nitrogen gas. The carbon source required during denitrification is formed by constituents from both the anaerobically treated condensate and the crude condensate mixed therewith.

20 Via a conduit 15 the liquid-sludge mixture comes into a nitrification unit 16 wherein the sludge-liquid mixture is aerated with air blown in via the line 17. The oxygen present in the air is used by the micro-organisms to convert ammonia into NO_2^- and NO_3^- . 95% of the content of the nitrification 25 unit is fed back via a conduit 19 provided with a pump 18 to the denitrification unit 14. Only 5% of the content of the nitrification unit is discharged to the settling tank 14 in which sludge and treated liquid are separated. The treated effluent leaves the settling tank 14 via the conduit 20. The 30 composition of the effluent is shown in table 4.

In the denitrification unit 14 the NO_3^- concentration lay between 10 and 20 mg/l during the test. At the beginning of the test the NO_3^- concentration even amounted for some time to 10 mg/l. The pH varied between 8.1 and 8.5.

35 In the nitrification unit the pH lay between 7.9 and 8.7. The oxygen content varied between 0.5 and 5.0 mg/l and had an average of 2.6 mg/l.

The sludge quality was satisfactory. The sludge content in the system amounted over the whole test to an average 4.0

gSS/l. The ash percentage of the solids was an average 23%, while the chemical oxygen demand of the sludge amounted to 1.2 gCOD/gSS. The sludge accretion amounted to an average of 0.14 gSS/S added COD, or 0.15 gCOD/g added COD.

5 Over the whole test the treating yield amounted to 99.8 BOD%.

For the cost-effectiveness of processing processes for manure it is important to separate as many valuable products as possible from the manure. Not only the sale price of these 10 valuable products is of importance but especially also the costs at which these products can be separated from the manure.

15 In processing processes known to date all attention has been devoted to separating solid matter from the manure, the so-called manure cake, which is a valuable fertilizer after 15 drying.

20 A first known processing process is the so-called Promest process, wherein the manure is first fermented in a fermentation installation in order to generate bio-gas. Subsequently separated from the fermented manure are the solids which after drying form a valuable product as manure cake. As a consequence of the fermentation practically all organic 20 compounds are degraded.

25 A second known processing process is described in the Netherlands patent application 87.00803 wherein bacteria are added to the manure or to a supernatant obtained by liquid-solids separation, which bacteria are capable of using the manure as substrate for the production of amino acids, such as L-lysine and L-methionine. As a result of the complex 30 composition of the substrate or of its supernatant which contains all manner of frequently disturbing organic and inorganic compounds, economically unacceptable high costs are required for recovering the formed amino acids in sufficiently pure form from the manure or the supernatant.

35 A third known processing process is the so-called Greenfield process (US-3.855.079, US-4.270.974 and US-4.608.120). According to this processing process a non-volatile oil is added to the manure and the oil slurry formed is dehydrated by evaporation under the influence of heat, whereafter

oil residues are removed from the formed condensate which can be discharged as effluent after biological treatment. The biogas formed during the biological degradation can be used in the processing process, see further "Natuur en Techniek" 5 57, 894-903 (1989).

The invention is based on the insight that the manure contains valuable carbon, energy and nitrogen sources which are separable from the manure in relatively pure state via the gas phase, since the carbon source, energy source and 10 nitrogen source can consist substantially of volatile compounds, such as lower fatty acids, namely acetate, and ammoniac. The nitrogen source and the carbon source are further present in practically ideal ratios with respect to the microbial synthesis of amino acids.

15 Another important advantage for the use of a substrate that is removed from manure via the gas phase is that the condensate is substantially sterilized and particularly clean, namely containing substantially no mineral salts. The condensate can thereby be adapted optimally to the conditions 20 required by the micro-organisms for producing organic compounds such as amino acids.

The invention thus provides a method for the synthesis of organic compounds from manure, comprising of:

- i) concentrating the manure;
- 25 ii) condensing the formed vapour;
- iii) adding to the condensate micro-organisms which are capable of producing the organic compound; and
- iv) separating from the condensate the organic compound produced by the micro-organisms.

30 The condensate can be split by fractional condensation into a first condensate that is relatively rich in ammonia (nitrogen source) and a second condensate relatively rich in organic compounds (carbon source and energy source). Depending on the micro-organisms to be used it is possible to 35 mix both the condensates in varying quantities whereby an optimal carbon/nitrogen ratio is obtained.

The concentration of ammonia in the condensate can be enlarged by concentrating the manure at a comparatively high pH, in general a pH of 5-7, preferably pH 6-7. The increasing

of the ammonia content in the condensate involves however a lowering of the fatty acid content in the condensate.

Another further possibility for optimal adaptation of the condensate is the concentrating of the condensate whereby 5 the required reaction volume, the efficiency of the production and the concentration of the organic compound in the condensate and separation of the formed organic compound are improved.

All the above mentioned preferred embodiments indicate 10 that the condensate can be maximally adapted to the conditions required by the micro-organisms for an optimal production of the organic compound.

It is further possible to add special additives to the condensate. In particular can be added minerals and metals 15 such as potassium, phosphate, magnesium, iron and manganese, vitamins, namely biotin and thiamine, a protein source, such as protein hydrolysate, for instance soya, casein or meat extract. A starch source, such as agricultural waste, molasses, whey and the like, can further be added.

20 Since the conditions required by the micro-organisms for producing the organic compound likewise comprise conditions for allowing growth of the micro-organisms themselves, it can be advantageous to allow the micro-organisms to increase in mass in a separate reactor, whereafter this biomass 25 is used in another reactor to produce the organic compound. The growth medium in the first reactor is preferably an enriched condensate. Therefore according to a variant of the method according to the invention, in a first reactor the micro-organisms are placed in contact with condensate 30 enriched with additives, and biomass of micro-organisms cultivated in the first reactor is brought into contact in a second reactor with condensate that may have been used in the first reactor.

The organic compounds which can be produced are 35 vitamins, such as B₆ and B₁₂, and amino acids such as L-lysine and/or L-methionine. Known micro-organisms which can produce these amino acids comprise the micro-organism species of the genera *Arthrobacter*, *Brevibacterium*, *Corynebacterium*, *Bacillus*, *Escherichia*, *Microbacterium*, *Micrococcus* and

Pseudomonas, see for example US-A-3.161.218, US-A-3.687.810, US-A-3.707. 441, US-A-3.825.472, US-A-3.905.867 and US-A-3.959.075.

The production with micro-organisms of the desired organic compound takes place in the liquid phase at a temperature lying generally between 0 and 70°C, more preferably between 15 and 50°C, such as around 30°C. Although production can take place in loads, it is recommended that the method be performed continuously, wherein a duration time in the reactor is maintained lying between 2 and 250 hours, in general between 5 and 200 hours. The quantity of organic compound produced depends on the conditions but lies for amino acid in general between 0.5-5 g amino acid per gram of ammonia; for instance, with sufficient ammonia in the condensate 80 to 90% of the theoretically maximum feasible fermentation efficiency can be achieved, such as for instance 40 g lysine per litre of condensate. The content of the initially present volatile organic compounds in the condensate, namely acetic acid and propionic acid, decreases herein within 2-3 days to less than 5% of the original content.

It is favourable if prior to concentrating the manure, but still more preferably immediately after the production of the manure, the manure is acidified. On the one hand, premature fermentation and degradation of the desired volatile, organic compounds is thereby avoided, and on the other hand odour problems are reduced and the transition of the volatile, organic compounds to for example the carrier oil used is promoted.

The method according to the invention can be applied to many types of manure, such as manure derived from cattle farms, pig farms, poultry farms and the like. Generally the manure may have a solids content of 7% but the method according to the invention is particularly suitable for manure with a higher solids content, such as preferably at least 10%, and more preferably to more than 14%. The advantage hereby results that in a central manure processing a smaller quantity of manure has to be transported and there results a

smaller quantity of condensate with a higher concentration of the desired volatile, organic compounds.

This method according to the invention will be described hereinafter with reference to two embodiments which 5 are focussed on the production of amino acids, namely L-lysine, with suitable micro-organisms, and which are shown schematically as flow diagrams in the figures 7 and 8.

Pig manure from which bulky waste is removed by sieves is subsequently acidified. The acidified manure is mixed with 10 a water insoluble paraffin liquid with a boiling point of circa 180°C. The mixture of manure and paraffin is concentrated in a concentrator, wherein the vapour formed is condensed in a condenser. The condensate 101 is fed to an extractor 102 to which an extraction mixture is fed via the 15 conduit 103. This extraction mixture consists of 40% sec-butyldioctylphosphine oxide and 60% n-dodecane.

A condensate is obtained making use of the Greenfield process. To this end pig slurry manure is acidified and mixed with an oil immiscible with water. This oil-manure mixture is 20 dehydrated by evaporation, whereafter oil residues are removed from the condensate. Depending on the degree of acidification (pH 4.5 to 7) the condensate contained 500 to 2000 ppm ammonia and further 5 to 20 kg/m³ of volatile organic 25 compounds, namely acetic acid, propionic acid, isobutyric acid, butyric acid and isovaleric acid. This condensate is used in the following experiments.

EXPERIMENT 1

The condensate is neutralized to pH 7.2 and used as water 30 phase in the preparing of a known lysine producing medium (LPM-medium). Added to this condensate-medium are lysine producing micro-organisms, whereafter 2 g lysine per litre of medium are produced within 30 hours. At the same time the ammonia concentration falls from 1.3 to 0.3 g/l. If the sugar 35 and ammonia sources are omitted from the LPM-medium, the same lysine production is obtained.

EXPERIMENT 2

Condensate (figure 7) is fed via a conduit 101 to a neutralizing device 102. After addition of nutrients via the conduit 103, the mixture is acidified to a pH of 7.2. The 5 acidified concentrate is fed via the conduit 104 to a reactor 105 in which the micro-organisms are immobilized on a carrier such as active carbon and alginate. In the reactor 105 the fermentation of the condensate is performed at a temperature of about 30°C, a pH of 7.2 and under aerobic conditions. The 10 through-flow of the reactor 105 is such that the micro-organisms were substantially not flushed.

Via the conduit 6 the biomass from the reactor 105 is fed to a separating device 107 wherein micro-organisms are separated which are optionally fed back via the conduit 108 15 to the reactor 105. The effluent is fed via conduit 109 to a unit in which the formed amino acid, in this case L-lysine, is selectively separated. For this purpose the separating unit contains an anion exchanger, for example Amberlite IR-120, in the H-form.

20 The through-flow is optionally fed via the conduit 111 to a water treatment but can in specific cases be immediately discharged.

The amino acid accumulated in the separating unit 110 25 is removed therefrom by elution via the elution inlets and outlets 112 and 113. The obtained lysine fraction can if desired be concentrated.

EXPERIMENT 3

Condensate (figure 8) is fed via a conduit 114 to a concentration unit 115 in which the substrate is partially concentrated by water extraction. A portion of the concentrated substrate is fed via the conduits 116 and 117 to a neutralizing device 118 to which nutrients are also fed via the conduit 119. The mixture of concentrated condensate and 35 nutrients is neutralized to pH 7.2. The condensate is subsequently fed to a reactor 120 in which micro-organisms are oculated. Through the specific composition of the condensate the micro-organisms will mainly grow and increase strongly in biomass. The increase in micro-organisms is fed

via a conduit 121 to another reactor 122. Further fed to this reactor 122 via the conduits 116 and 123 is concentrated condensate from the concentration device 115. Used condensate that leaves the reactor 120 via the conduit 124 can 5 optionally also be fed to the reactor 122.

In the reactor 122 the condensate serves as substrate for the micro-organisms for the production of the amino acid, namely l-lysine or l-methionine. The mass which leaves the reactor 122 via the conduit 125 is filtered in the separating 10 unit 126 into a biomass fraction which is fed back via the conduit 127 to the reactor 122. The liquid phase is fed via the conduit 128 to the separating unit 129, in which, as described in experiment 2, the produced amino acid is separated and finally discharged via the conduit 130. The 15 exhausted condensate leaves the separating unit 129 via the conduit 131 and is preferably first treated prior to being discharged.

For the cost-effectiveness of processing processes for manure it is important to separate as many valuable products 20 as possible from the manure. Not only the sale price of these valuable products is of importance but especially also the costs at which these products can be separated from the manure.

In processing processes known to date all attention has 25 been devoted to separating solid matter from the manure, the so-called manure cake, which is a valuable fertilizer after drying.

A first, known processing process is the so-called Promest process, wherein the manure is first fermented in a 30 fermentation installation in order to generate bio-gas. Subsequently separated from the fermented manure are the solids which after drying form a valuable product as manure cake. As a consequence of the fermentation practically all organic compounds are degraded.

35 A second known processing process is the so-called Greenfield process (US-3.855.079, US-4.270.974 and US-4.608. 120). According to this processing process a non-volatile oil is added to the manure and the oil slurry formed is dehydrated by evaporation under the influence of heat,

whereafter oil residues are removed from the formed condensate which can be discharged as effluent after biological treatment. The biogas formed during the biological degradation can be used in the processing process, see 5 further "Natuur en Techniek" 57, 894-903 (1989).

The invention is based on the insight that present in manure are valuable, volatile organic compounds which are economically separable from the manure if condensate is removed from the manure without prior fermentation thereof and 10 this condensate is subjected to a suitable physico-chemical separation process for separating the volatile organic compounds. These compounds can be separated since on the one hand they are organic and on the other hand they are volatile. The organic character makes it possible to separate 15 them from inorganic components in the manure, for example by means of the used oil as carrier liquid, and the volatile character makes it possible to separate them from non-volatile organic compounds which will remain behind in the oil.

20 The invention thus provides a method for recovering volatile, organic compounds from manure, which is characterized in that the method comprises:

- i) concentrating the manure;
- ii) condensing the formed vapour; and
- 25 iii) separating volatile, organic compounds from the condensate.

Suitable volatile, organic compounds are largely compounds with one to six carbon atoms, in particular however volatile fatty acids such as acetic acid, propionic acid, 30 butyric acid, isobutyric acid, valeric acid and isovaleric acid. These organic compounds are not only valuable, they are also present in relatively large quantities in the condensate. A usual condensate contains for example per m³ 8-11 kg acetic acid, 1-5 kg propionic acid, 0.2-1 kg isobutyric 35 acid, 0.5-1.5 kg butyric acid and 0.2-0.7 kg isovaleric acid.

With the method according to the invention it is possible to recover these volatile, organic compounds and the added value of these organic compounds to the manure proces-

sing process is greater than that of biogas that may be formed from these organic compounds.

The separating of the volatile, organic compounds from the condensate can take place according to many known 5 physico-chemical methods.

A reliable, relatively simple and economic method is liquid extraction.

A number of extraction agents are particularly preferable because of their low cost-price, high volatility 10 and high distribution co-efficients in equilibrium.

A first group of favourable extraction agents comprises organic alkylphosphine oxides. Particularly suitable are the trialkylphosphine oxides such as trioctylphosphine oxide, trihexylphosphine oxide, sec-butyldioctylphosphine or 15 mixtures thereof. In this context reference is made to the European patent applications EP-A-132.700 and EP-A-259.583, which describe liquid extractions wherein the alkylphosphine oxides are used as extraction agents. The liquid extraction methods described all relate only to the removal of carbonic 20 acids, aldehydes, ketones, alcohols and phenols from waste flows which are for example released during the preparation of cellulose, phenol and the Fischer-Tropsch process.

Another group of suitable extraction agents is the group of higher alkylamines. Preferred are trialkylamines, in 25 particular trioctylamine and di-tridecylamine. For further information regarding the use of amines in liquid extraction reference is made to N.L.Ricker et al, J. Separ. Proc. Technol. 1, 23-30, (1980).

A polar solvent is preferably added to the extraction 30 agent whereby the extraction efficiency for the volatile, organic compounds for separation improves. Suitable polar solvents are alcohol, such as ethylhexanol, halogenated hydrocarbons, such as chloroform, esters, and ketones, such as diisobutyl ketone and cyclohexanone.

35 Other methods for separating volatile, organic compounds, optionally after prior concentration for instance by evaporation or reversed osmosis, comprise distillation, ion exchange and crystallization. In the case of crystalli-

zation the corresponding, poorly water-soluble salts such as calcium salts can be separated.

It is favourable if prior to concentrating the manure, but still more preferably immediately after the production of 5 the manure, the manure is acidified. On the one hand, premature fermentation and degradation of the desired volatile, organic compounds is thereby avoided, and on the other hand odour problems are reduced and the transition of 10 the volatile, organic compounds to for example the carrier oil used is promoted.

The method according to the invention can be applied to many types of manure, such as manure derived from cattle farms, pig farms and poultry farms and the like. Generally the manure may have a solid content of 7% but the method 15 according to the invention is particularly suitable for manure with a higher solid content, such as preferably at least 10%, and more preferably to more than 14%. The advantage hereby results that in a central manure processing a smaller quantity of manure has to be transported and there 20 results a smaller quantity of condensate with a higher concentration of the desired volatile, organic compounds.

The method according to the invention will be described hereinafter with reference to two embodiments which are shown schematically as flow diagrams in the figures 9 and 10.

25 Pig manure from which bulky waste is removed by sieves is subsequently acidified. The acidified manure is mixed with a water insoluble paraffin liquid with a boiling point of circa 180°C. The mixture of manure and paraffin is concentrated in a concentrator, wherein the vapour formed is 30 condensed in a condenser. The condensate 201 is fed to an extractor 202 to which an extraction mixture is fed via the conduit 203. This extraction mixture consists of 40% sec-butyldioctylphosphine oxide and 60% n-dodecane.

35 The treated condensate 204 is fed to a biological after-treatment installation. The loaded extraction liquid is fed via the conduit 205 to a dehydrator 206 wherein using steam supplied via the conduit 207 water is removed from the loaded extraction liquid and fed back to the extractor 202 via the conduit 208.

The loaded extraction liquid with the water removed is fed to a distillation column 210. The distillation column can carry out a fractional distillation, whereby the more volatile, organic compounds leave the distillation column at 5 a higher level. Operating at a pressure of 0.2 bar and a pot temperature of 135°C, isovaleric acid, butyric acid, isobutyric acid, propionic acid and acetic acid can be successively fractionated. The extraction agent stripped of the volatile, organic compounds is fed via the conduit 211 to the extractor 10 202 via the conduit 203, optionally supplemented with fresh extraction agent via the conduit 212.

If necessary a number of the lower-boiling organic compounds can be carried away via the conduit 213 to the condensate conduit 204 for further degradation in the biological 15 treatment installation. Finally, it is possible to feed back a portion of the condensate from the conduit 204 via the conduit 214 to the condensate feed conduit 201.

In the second embodiment of the method according to the invention condensate is fed via the conduit 201 to an extractor 215 to which an extraction agent is further supplied via the conduit 216. This extraction agent consists of a mixture of a tertiary amine with a mean molecular weight of approximately 392 (Alamine 336 of General Mills Inc.), and 60% ethylhexanol.

25 The extracted condensate leaves the extractor 215 via the conduit 217. The loaded extraction mixture is fed via the conduit 218 to a second extractor 219 to which a watery alkaline solution (for example, 0.5N caustic soda) is fed via the conduit 220. The extraction agent leaves the extractor 30 219 via the conduit 21 and is optionally supplemented via the conduit 222 with fresh extraction agent fed to the extractor 215 via the conduit 216. The product flow leaves the extractor 215 via the conduit 223. This product flow contains a solution of sodium salts of C₂-C₅ fatty acids. This mixture 35 can subsequently be separated into the various compounds with known, usual separating methods.

If required, a portion of the treated condensate can be fed back to the extractor 215 via the conduit 224. It is

further possible that the product flow be fed via the conduit 224 to the second extractor 219.

Although the present invention is particularly concentrated on the separating of the volatile, lower alkyl-carbonic acids, it is also possible using the described method according to the invention to separate lower alkylalcohols, lower alkylesters, lower alkylketones and lower alkylaldehydes from the manure, to the extent that their presence makes this economically worthwhile.

It is of importance for the cost-effectiveness of treating processes for manure to separate as many valuable products as possible out of the manure. An optimal balance has of course to be sought here between on the one hand the costs of the process and on the other hand the return on the sales of the products.

A per se known treating process which enables the separation of useful products from the manure in economic manner is the so-called Greenfield process. This is described in the American patents 3 855 079, 4 270 974 and 4 608 120, among others. In this known process a carrier liquid such as a non-volatile oil is added to the manure which displaces the water out of the manure because the water evaporates through the effect of heat. The carrier liquid is then removed through evaporation and purified for re-use. The carrier liquid also serves as extraction agent for the fats originally present in the manure. These are released as manure fat during the purifying of the carrier liquid vapour.

This manure fat which is released as a product of the process in a quantity of approximately 10% of the initial amount of manure based on the dry substance content, can for instance be re-used in mixed fodder. Another possibility is the conversion of the manure fat into high-grade protein.

In the light of the above the invention has for its object to embody a method of the type specified in the preamble such that a high economic efficiency is achieved.

This object is achieved with the method according to the invention by burning the manure fat in a controlled manner and at least partially using the energy thereby released in the manure treating process.

According to a first embodiment of the invention this can be carried out by burning the manure fat in a boiler wherein a heat transporting medium used in the process is heated. By burning the recovered manure fat roughly 50% of 5 the thermal energy requirement for the manure treating can be covered. The saving achieved herewith is considerable.

The manure fat is preferably burned at a flame temperature of a maximum of 1100°C. It has been found that any possible problems with respect to slag deposition in the 10 burner and boiler can hereby be avoided. It generally is desirable to take steps for cooling the flame formed during the burning.

In accordance with the specific conditions whereunder the manure treating process is carried out, the manure fat 15 can contain quite a large quantity of solid constituents with a very small particle size. During burning these solid constituents are released as dust ash. In order to prevent the boiler becoming rapidly dirtied by the dust ash, and therefore to avoid regular operational stoppage for cleaning 20 of the boiler, according to the preferred embodiment of the method according to the invention the dust is removed from the flue gases directly after burning and the cleaned flue gases are carried further to the heat exchanger part of the boiler to heat the heat transporting medium.

25 In a very favourable further development of the invention the manure fat is burned in a diesel engine and the heat of the cooling agent and the exhaust gas of the diesel engine are used for heating a heat transporting medium that is used further in the manure treating process. The 30 mechanical energy produced by the diesel engine during burning of the manure fat can for instance be used for driving conveyors, pumps and the like. The mechanical energy is however preferably converted into electrical energy which is at least partially re-used for driving electro-motors 35 active in the process. As a result of the thus realized combined heat-power production, energy cost savings that are more than four times greater can be achieved than with the burning of the manure fat in a boiler. An additional advantage of this further development of the invention is that the

legal requirements imposed on exhaust gases of diesel engines with respect to the emission of harmful substances are less strict than on the discharge gases of combustion boilers. The necessary investment for cleaning the exhaust gases can 5 therefore be lower.

The invention also relates to and provides a device for treating manure comprising means for extracting from the manure fats present therein such as manure fat, a burning device for the manure fat which comprises heat transfer means 10 for transferring heat released during the burning to a heat transporting medium.

In a first embodiment of the device according to the invention the burning device comprises a combustion boiler having a burner to which manure fat can be fed and a heat 15 exchanger through which can flow heat transporting medium. The thermal energy is used in the manure treating device for example for dehydrating the manure by evaporation.

The burner preferably comprises means for cooling the flame. These means can for instance be embodied such that 20 steam or water is injected herewith into the flame. Another possibility is to mount the burner in a water-cooled furnace tube. The flame can then rapidly transfer heat to the relatively cool wall of the furnace tube through radiation.

The boiler is preferably embodied as a fire tube 25 boiler. Since a relatively large quantity of ash constituents can be released during burning of manure fat, the boiler can quickly become dirtied. A fire tube boiler has in contrast to a water tube boiler the advantage that it can be cleaned quickly.

30 Another favourable embodiment of the combustion boiler is one wherein a heat resistently walled cyclone for separating dust is arranged between the burner and the heat exchanger. Because a consider-able portion of the dust ash formed during burning of the manure fat can be separated from 35 the hot flue gases, the heat exchanger of the boiler connected thereafter remains to a considerable extent free of dirt so that the cleaning frequency will be markedly lower.

In a further development of the device according to the invention wherein the burning device is a combustion boiler,

a filtering device for the manure fat is employed which can remove very small particles from the manure fat. An ultra-centrifuge can for instance be used which can separate particles greater than 1 μm out of the manure fat. By 5 treating the manure fat beforehand in the filtering device, a significant portion of the solid particles is removed so that no, or practically no, dust ash is formed during burning and dirtying of the boiler is thus greatly reduced.

According to a very favourable further development of 10 the device according to the invention the burning device comprises a diesel engine of the type that is suitable for burning heavy fuel oil. The heat transfer means comprise therein cooling liquid and exhaust gas coolers. The released heat is again guided to determined points in the manure 15 treating process by means of a heat transporting medium. In order also to avoid any possible problems with a diesel engine with regard to dirtying, the manure fat can here also be purified beforehand of solid constituents in a suitable manner, or a manure treating process can be performed such 20 that only a small quantity of solid constituents occurs in the manure fat.

As is known, a diesel engine provides roughly a third of the energy present in the fuel as mechanical energy.

According to a favourable embodiment of the device according 25 to the invention this mechanical energy can be converted into electrical energy because an electrical generator is coupled to the diesel engine. The provided electrical energy can be used for a considerable part in the manure treating installation for driving pumps, conveyors and the like. Any 30 surplus of electrical energy can be delivered to the consumer electricity grid, for payment of course.

Since use can be made of components known per se the above description provides a person skilled in the art sufficient information to be able to use the invention.

Table 1: Fertilizer granulates according to the invention

	0	1	2	3	4	5	6
5 Fertilizer (kg)	-	2,5	2	2	25	25	25
Binder (kg)	-	-	-	-	-	-	-
chalk 30%H ₂ O			2,85				
molasse				1,74			
CMC					2		
10 Bentonite						2,5	
Water (l)	-	1,4	1,23	0,87	17,5	11,2	15
Moisture (%)	1,5	32,5	36,4	32,4	31	31,4	33,2
Granulate distribution (%)							29
8 mm	-	-	-	-	0,9	-	6,3
15 6 mm	-	1,5	-	0,6	8	3	7,7
5 mm	-	8	0,9	1,4	19	10	12
3 mm	-	28	6,5	15	39	29	59
2 mm	0,2	53	42	72	54	75	82
1 mm	2	89	93	96	84	84	93
20 0,5 mm	22	99,3	99,1	99,4	98,5	96,3	99,1
<0,5 mm	-	0,7	0,9	0,6	1,5	3,7	0,9
0,2 mm	58	-	-	-	-	-	-
0,1 mm	72	-	-	-	-	-	-
<0,1 mm	27	-	-	-	-	-	-

Table 2

Analysis	N-Fertilizer	S-Fertilizer
Dry matter	84,3	97,2
NH ₄ -N	1,76	2,60
NO ₃ -N	3,03	2,10
N-total	6,90	7,81
P ₂ O ₅ -total	2,80	3,39
K ₂ O-total	5,28	7,99
Organochloropesticides (mg/kg)	< 10	< 10
Polychlorobiphenyls (mg/kg)	< 10	< 10
Cadmium (mg/kg)	< 1	< 1
Chromium (mg/kg)	39	47
Copper (mg/kg)	225	245
Mercury (mg/kg)	0,1	0,1
Nickel (mg/kg)	21	14
Lead (mg/kg)	< 10	< 10
Zinc (mg/kg)	340	345
Arsenic (mg/kg)	1,1	0,8

TABLE 3

	manure	conden- sate	conden- sate + nutrient solution
COD (mg/l)	150,000	7,300	7,300
NH ₄ -N (mg/l)	6,000	300	620
P-total	2,100	37	76
Cl (mg/l)	3,400	60	--
K (mg/l)	6,900	--	--
Acetic acid (mg COD/l)	17,600	4,500	4,500
Propionic acid (mg COD/l)	7,600	1,800	1,800
Isobutyric acid (mg COD/l)	1,600	400	450
Butyric acid (mg COD/l)	6,600	1,200	1,200
Isovaleric acid mg COD/l)	600	770	770
Valeric acid (mg COD/l)	--	140	140

TABLE 4

	crude condensate	anaerobically treated condensate	anaerobically treated + 10% crude condensate	effluent
BOD (mg/l)	18,500	120	2,000	< 15
COD (mg/l)	25,900	430	3,000	< 100
NH ₄ -N (mg/l)	790	320	370	< 1
P (mg/l)	--	38	34	≤ 25
K (mg/l)	--	160	--	--
pH	4.0	7.9	--	--
NO ₂ - (mg/l)	--	--	--	< 20
NO ₃ - (mg/l)	--	--	--	< 25

CLAIMS

1. Method for preparing a granular fertilizer from manure, comprising the steps of:

- i) acidifying the manure;
- ii) dehydrating the acidified manure and evaporating the carrier liquid; and
- iii) forming granules from the fertilizer obtained.

5 2. Method as claimed in claim 1, wherein the manure is acidified using nitric acid.

10 3. Method as claimed in claim 1 or 2, wherein the manure is acidified using sulphuric acid.

4. Method as claimed in claim 2 or 3, wherein the manure is acidified using a mixture of nitric acid and sulphuric acid.

15 5. Method as claimed in claim 4, wherein in the mixture the nitric acid to sulphuric acid is 30-50:70-50.

6. Method as claimed in claim 5, wherein the nitric acid to sulphuric acid ratio is 35-45:65-55.

7. Method as claimed in claim 1-6, wherein 1-10% by weight acid is added to the manure.

20 8. Method as claimed in claim 7, wherein 1-5% by weight, preferably 3% by weight acid is added to the manure.

9. Method as claimed in claim 7 or 8, wherein the manure is acidified to a pH of 3.5-5.5, preferably to 4-5, more preferably to 4.1-4.3.

25 10. Method as claimed in claim 9, wherein the manure is acidified shortly after its production.

11. Method as claimed in claim 1-10, wherein additives, such as sulphates, nitrates and potassium salts, are added to the fertilizer.

30 12. Method as claimed in claim 1-11, wherein the manure is granulated.

13. Method as claimed in claim 12, wherein granulation promoting agents are added.

14. Method as claimed in claim 13, wherein the granulation promoting agents are selected from the group comprising chalk, molasses, carboxymethyl cellulose, bentonite.

5 15. Method as claimed in claim 10-14, wherein the granulate is dried using vacuum cooling.

16. Method as claimed in claim 10-15, wherein the dry mature content of the granulate is more than 80%, preferably more than 85%, more preferably more than 90%.

10 17. Method as claimed in claim 1-16, wherein the granulate comprises:

$\text{NH}_4\text{-N1}$ - 3 % by weight

$\text{NO}_3\text{-N1,5}$ - 3,5 % by weight

N-total5 - 9 % by weight

15 $\text{P}_2\text{O}_5\text{-total2}$ - 5 % by weight

$\text{K}_2\text{O}\text{-total3}$ - 10 % by weight

18. Method as claimed in any of the preceding claims, wherein an organic carrier liquid is added to the manure acidified, the mixture comprising manure and carrier liquid 20 is dehydrated by evaporation, and the carrier liquid is evaporated from the fertilizer.

19. Method for processing manure, comprising the steps of:

- i) adding an organic carrier liquid to the manure;
- 25 ii) concentrating the mixture of manure and carrier liquid;
- iii) condensing the formed vapour;
- iv) anaerobic treating of the condensate; and
- v) aerobic treating of the effluent from the 30 anaerobic treatment.

20. Method as claimed in claim 19, wherein prior to concentrating the manure is acidified.

21. Method as claimed in claim 19 or 20, wherein a portion of the effluent from the anaerobic treatment is 35 recirculated and mixed with condensate for treating.

22. Method as claimed in claim 21, wherein 20-90%, preferably 30-80%, and more preferably 40-80% of the effluent is recirculated.

23. Method as claimed in claims 19-22, wherein a nutrient preparation is added to the condensate.

24. Method as claimed in claim 23, wherein the nutrient preparation supplements for a nitrogen requirement of at 5 least 50 g/m³, preferably 60 g/m³, and more preferably 70-80 g/m³.

25. Method as claimed in claim 23 or 24, wherein the nutrient preparation supplements for a phosphorus requirement of at least 10 g/m³, preferably 15 g/m³, and more preferably 10 20 g/m³.

26. Method as claimed in claims 23-25, wherein the nutrient preparation contains trace elements.

27. Method as claimed in claims 19-26, wherein the anaerobic treatment achieves a COD processing yield of more 15 than 80%, preferably 85%, more preferably 90%, such as 90-95%.

28. Method as claimed in claims 19-27, wherein in the anaerobic treatment sludge is used derived from the treatment of waste water from alcohol preparation and/or paper preparation. 20

29. Method as claimed in claim 28, wherein the sludge is adapted to the degradation of C_n fatty acids, wherein n≥2.

30. Method as claimed in claims 19-29, wherein the effluent deriving from the anaerobic treatment is denitrified 25 in a denitrification unit and nitrified in a nitrification unit, and wherein a portion of the sludge-influent mixture from the nitrification unit is recirculated to the denitrification unit.

31. Method as claimed in claim 30, wherein the 30 recirculation ratio for the sludge-influent mixture amounts to 10-30, preferably 15-25, such as 20.

32. Method as claimed in claim 30 or 31, wherein crude condensate is added to the influent.

33. Method as claimed in claim 32, wherein the influent 35 contains 1-20%, preferably 5-20% and more preferably 10-15% crude condensate.

34. Method as claimed in claims 30-33, wherein sludge from the nitrification unit is pre-mixed with the influent.

35. Method as claimed in claims 30-34, wherein the treating yield is greater than 90%, preferably greater than 95%, such as 97-99% BOD.

36. Method for producing organic compounds, such as 5 amino acids, from manure, comprising of:

- i) concentrating the manure;
- ii) condensing the formed vapour;
- iii) adding to the condensate micro-organisms which are capable of producing the organic compound; and
- iv) separating from the condensate the organic compound produced by the micro-organisms.

37. Method as claimed in claim 36, wherein the manure is condensed fractionally to a first ammonia-rich condensate and a second condensate rich in organic compounds.

38. Method as claimed in claim 36 or 37, wherein the manure is concentrated at a pH of 5-7, preferably pH 6-7.

39. Method as claimed in claims 36-38, wherein the formed condensate is concentrated.

40. Method as claimed in claims 36-39, wherein additives are added to the substrate.

41. Method as claimed in claim 40, wherein the additives comprise vitamins, metals, minerals, bulk substrate, agricultural waste.

42. Method as claimed in claims 36-41, wherein in a 25 first reactor the micro-organisms are placed in contact with medium enriched with additives and wherein the biomass of micro-organisms cultivated in the first reactor is brought into contact in a second reactor with condensate.

43. Method as claimed in claim 42, wherein in the first 30 reactor the micro-organisms are placed in contact with condensate enriched with additives.

44. Method as claimed in claims 36-43, wherein the condensate contains 5-20 g/l of carbon source and 0.5-5 g/l nitrogen source.

45. Method as claimed in claims 36-44, wherein the 35 produced organic compound is an amino acid.

46. Method as claimed in claim 45, wherein the amino acid is L-lysine and/or L-methionine.

47. Method as claimed in claims 36-46, wherein the micro-organisms comprise species of the genera *Arthrobacter*, *Brevibacterium*, *Corynebacterium*, *Bacillus*, *Escherichia*, *Microbacterium*, *Micrococcus* and *Pseudomonas*.

5 48. Method for recovering volatile, organic compounds from manure, comprising:

- i) concentrating the manure;
- ii) condensing the formed vapour; and
- iii) separating the volatile, organic compounds from the condensate.

10 49. Method as claimed in claim 48, wherein the volatile, organic compounds are removed from the condensate by liquid extraction.

15 50. Method as claimed in claim 49, wherein the extraction agent is an organic alkylphosphine oxide.

51. Method as claimed in claim 50, wherein the extraction agent is a trialkylphosphine oxide.

20 52. Method as claimed in claim 50 or 51, wherein the extraction agent comprises trioctylphosphine oxide, trihexylphosphine oxide, sec-butyldioctylphosphine oxide or mixtures thereof.

53. Method as claimed in claims 49-52, wherein the extraction agent is a higher alkylamine.

25 54. Method as claimed in claim 53, wherein the alkylamine is a trialkylamine.

55. Method as claimed in claim 53 or 54, wherein the trialkylamine comprises trioctylamine and di-tridecylamine.

30 56. Method as claimed in claims 49-55, wherein the liquid extraction takes place in the presence of a polar solvent.

57. Method as claimed in claim 56, wherein the solvent comprises alcohol, halogenated hydrocarbon, esters, ketones.

35 58. Method as claimed in claim 48, wherein the volatile, organic compounds are separated by crystallization, distillation and/or ion exchange.

59. Method as claimed in claims 48-58, wherein the manure to be concentrated is acidified.

60. Method as claimed in claims 48-59, wherein the manure to be concentrated has a dry solid content of at least

7%, preferably at least 11%, more preferably to more than 14%.

61. Method as claimed in claims 48-60, wherein the volatile, organic compounds to be recovered comprise C1-C5 fatty acids.

62. Method for treating manure comprising the drying of manure by displacing water out of the manure by a carrier liquid, extracting the carrier liquid by evaporation and purifying the carrier liquid vapour for re-use, wherein fats originally present in the manure are released as manure fat, by burning the manure fat in a controlled manner and at least partially using energy thereby released in the process.

63. Method as claimed in claim 62, wherein the manure fat is burned in a boiler wherein a heat transporting medium used in the process is heated.

64. Method as claimed in claim 63, wherein the manure fat is burned at a flame temperature of a maximum of 1100°C.

65. Method as claimed in claim 63, wherein combustion air is supplied in stages.

66. Method as claimed in claim 63, wherein dust is removed from the flue gases directly after burning and the heat transporting medium is heated with the cleaned flue gases.

67. Method as claimed in claim 62, wherein the manure fat is burned in a diesel engine and heat of a cooling agent and exhaust gas of the diesel engine is used for heating a heat transporting medium used in the process.

68. Method as claimed in claim 67, wherein mechanical energy produced by the diesel engine is converted into electrical energy which is at least partially used for driving electro-motors operative in the process.

69. Device for treating manure comprising means for extracting from the manure fats present therein such as manure fat, a burning device for the manure fat which comprises heat transfer means for transferring heat released during the burning to a heat transporting medium.

70. Device as claimed in claim 69, wherein the burning device comprises a combustion boiler having a burner to which

the manure fat can be fed and a heat exchanger through which can flow the heat transporting medium.

71. Device as claimed in claim 70, wherein the burner comprises means for cooling a flame produced by the burner.

5 72. Device as claimed in claim 70, wherein the boiler is a fire tube boiler.

73. Device as claimed in claim 70, wherein a heat resistantly walled cyclone for separating dust is arranged between the burner and the heat exchanger.

10 74. Device as claimed in claim 70, comprising a filtering device for the manure fat such as an ultra-centrifuge, for separating particles greater than 1 μm out of the manure fat..

15 75. Device as claimed in claim 69, wherein the burning device comprises a diesel engine of the type that is suitable for burning heavy fuel oil and wherein the heat transfer means comprise cooling liquid and exhaust gas coolers.

76. Device as claimed in claim 74, wherein the diesel engine is drivably coupled to an electrical generator.

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CLAY SOIL

-  artificial fertilizer
-  N-fertilizer
-  S-fertilizer

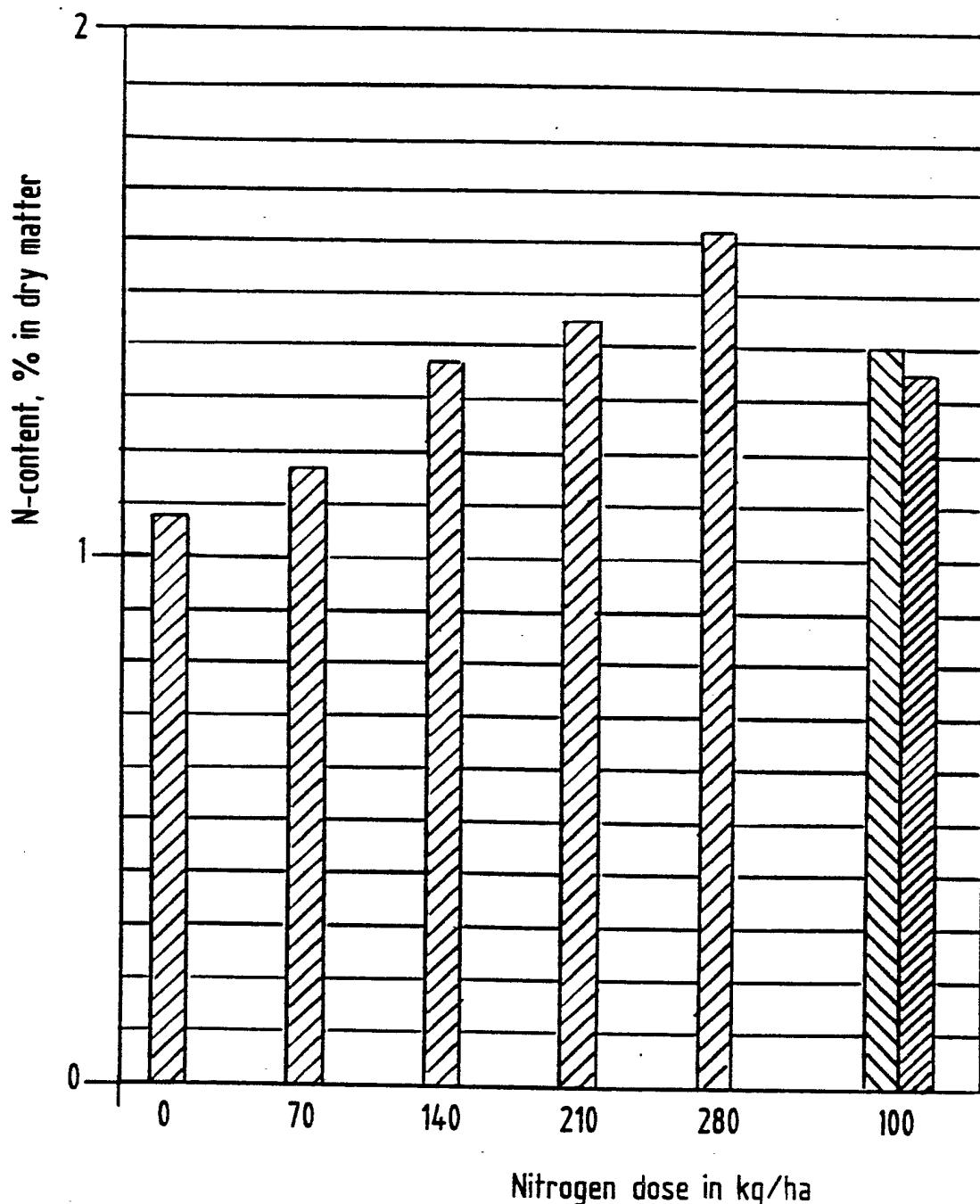
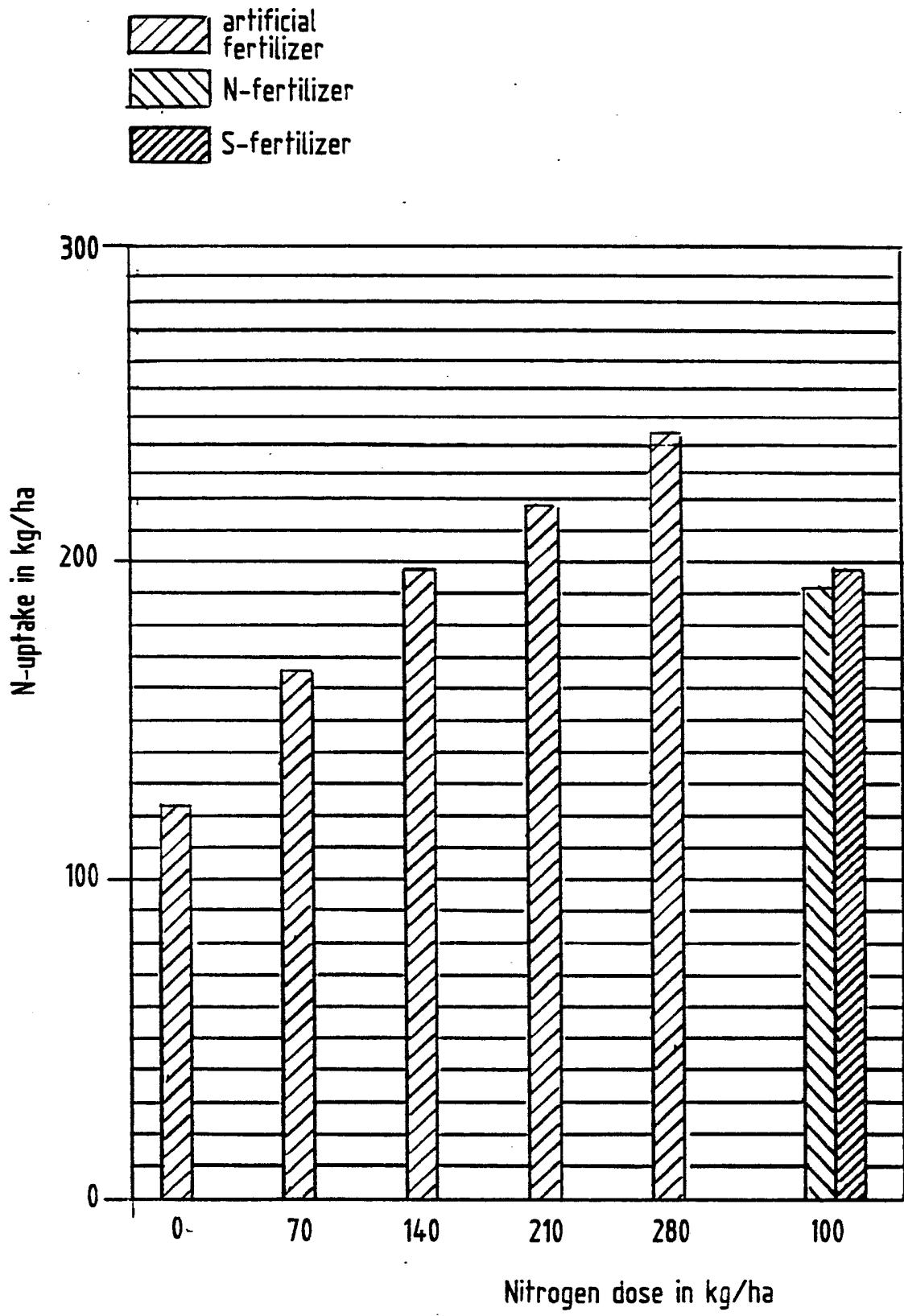


FIG. 1

SUBSTITUTE SHEET

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CLAY SOIL

FIG.2

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SAND SOIL

artificial
fertilizer

N-fertilizer

S-fertilizer

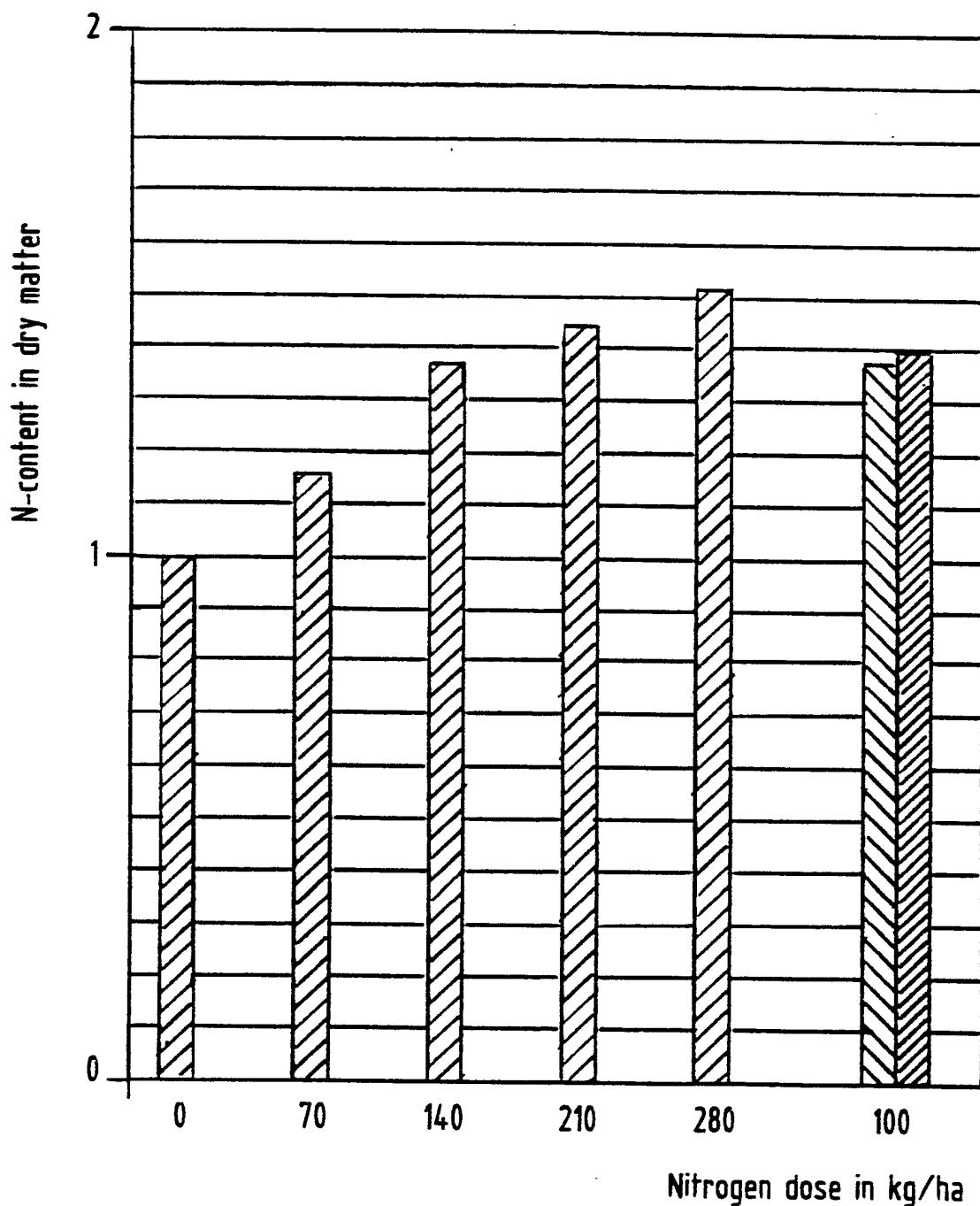


FIG.3

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SAND SOIL

artificial
fertilizer

N-fertilizer

S-fertilizer

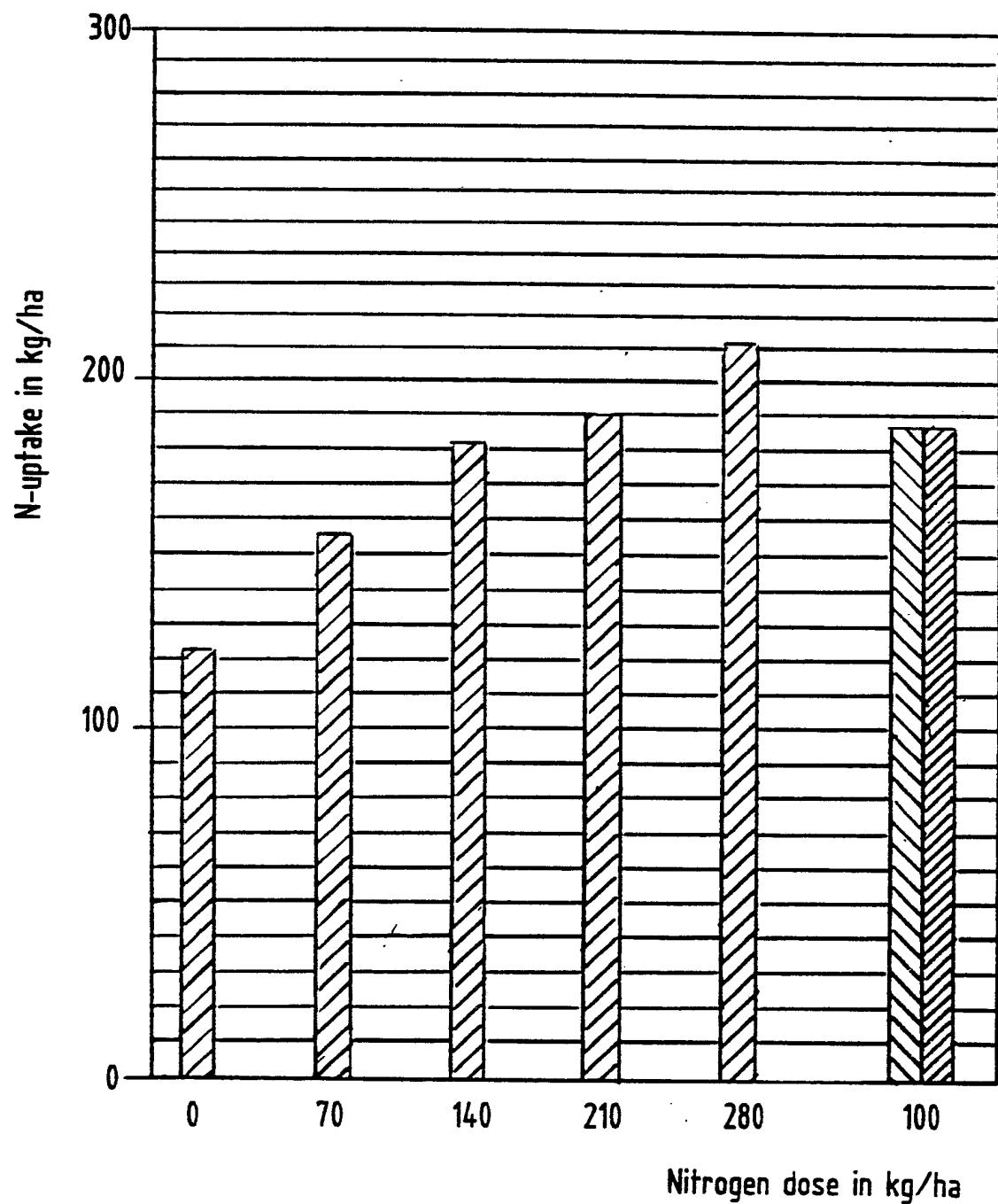


FIG. 4

